Fuel 133 (2014) 292–298

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Liquid–liquid equilibrium data for systems containing Brazil nut biodiesel + methanol + glycerin at 303.15 K and 323.15 K

Jefferson D. Gonçalves [a], Martín Aznar [b], Geormenny R. Santos [a,*]

[a] School of Chemical Engineering, Federal University of Pará, Campus of Guamá, Belém, PA 66075-110, Brazil
[b] School of Chemical Engineering, University of Campinas, Av. Albert Einstein 500, Campinas, SP 13083-852, Brazil

HIGHLIGHTS

- The biodiesel was obtained by alkaline transesterification with methanolic NaOH.
- Brazil nut biodiesel was characterized within the Brazilian standard norm.
- LLE data were measured for ternary systems at two temperatures.
- The Othmer–Tobias correlation was used to ascertain the quality of the tie-lines.
- The experimental data were correlated with the NRTL and UNIQUAC models.

ARTICLE INFO

Article history:
Received 21 February 2014
Received in revised form 25 April 2014
Accepted 5 May 2014
Available online 23 May 2014

Keywords:
Brazil nut biodiesel
Methanol
Glycerin
Liquid–liquid equilibrium

ABSTRACT

Due to the amount of compounds involved in the biodiesel production, liquid–liquid equilibrium data are essential in order to predict the proportions in which these compounds exist and subsequently proceed with a more efficient purification and aid in the design of the reactor and ponds. In this study, biodiesel was obtained through the basic transesterification of Brazil nut (*Bertholletia excelsa*) oil with methanol. Afterwards, the phase equilibrium behavior of this Brazil nut biodiesel + methanol + glycerol system was determined at $T = 303.15$ and 323.15 K and atmospheric pressure. The solubility curves were determined by the cloud-point method in isothermal conditions. The liquid-phases compositions were measured by determining their refractive index and densities. The Othmer–Tobias correlation was used to ascertain the quality of the experimental tie-lines. The results were correlated with the NRTL and UNIQUAC activity coefficient models. The calculated data showed good agreement with the experimental results, yielding a mean quadratic deviation in the composition of 1.49% and 1.18% using NRTL at 303.15 and 323.15 K, respectively, and 1.85% and 1.97% using UNIQUAC at 303.15 and 323.15 K, respectively.

1. Introduction

The search for clean energy has led to intense research on alternative energy sources, specifically aiming to replace fossil fuels. Biodiesel is the most promising result achieved so far since it is fully renewable. Biodiesel is a mixture of alkyl esters most commonly obtained through the transesterification of vegetable oil or animal fat.

In this reaction, a triacylglycerol reacts with an alcohol, usually a short-chain alcohol, in the presence of a catalyst (acid, basic, or enzymatic), forming two products, namely alkyl ester and glycerol. The mixture of alkyl esters obtained with this process, after separation and purification, constitutes the so-called biodiesel. This fuel can be used in diesel-cycle internal combustion engines without any modifications. In order for the process to be competitive, the reaction must have a high yield and low cost and generate no toxic byproducts [1].

After the transesterification reaction, two liquid phases are formed: a heavier, glycerin-rich one and a lighter, biodiesel-rich one. The excess unreacted alcohol is distributed between the two liquid phases. This way, the phase equilibrium of biodiesel + methanol + glycerin must be known since the representation of the real behavior of this mixture is essential for the design, operation, and optimization of the separation processes [2].

In the literature, the phase equilibrium of ternary systems with biodiesel or ester, glycerol, and alcohol has been reported by

* Corresponding author. Tel.: +55 91 3201 7291.
E-mail addresses: maznar@feq.unicamp.br (M. Aznar), geormenny@ufpa.br (G.R. Santos).

http://dx.doi.org/10.1016/j.fuel.2014.05.004
0016-2361/

several authors. Rostami et al. [1] modeled the experimental data for the systems canola biodiesel + methanol + glycerol and sunflower biodiesel + methanol + glycerol with the UNIQUAC model at 293.15, 303.15, and 313.15 K, Bell et al. [2] studied the liquid–liquid equilibrium for systems consisting of a methyl ester + glycerin + water at 333.15 K, and the experimental data were correlated with the NRTL model, Basso et al. [3] modeled data obtained experimentally for the macauba biodiesel + ethanol + glycerin system using the NRTL, UNIQUAC, and UNIFAC-Dortmund models, Mazutti et al. [4] modeled the experimental data with the UNIQUAC model for binary, ternary, and quaternary systems containing soy biodiesel, methanol/ethanol, water, and glycerin at 303.15, 318.15, and 333.15 K, Silva et al. [5] obtained experimental data for the binary, ternary, and quaternary systems consisting of ethyl esters (FAEE) and methyl esters (FAME) of *Jatropha curcas*, water, glycerin, methanol, and ethanol at 303.15, 318.15, and 333.15 K, using the UNIQUAC model for correlation.

The goal of this study was to obtain biodiesel from the basic transesterification of Brazil nut (*Bertholletia excelsa*) oil with methanol and to study the liquid–liquid equilibrium of the ternary system containing Brazil nut biodiesel + methanol + glycerin. Binodal curves and tie-lines were determined at 303.15 and 323.15 K. The results were well correlated with the NRTL and UNIQUAC activity coefficient models.

2. Materials and methods

2.1. Transesterification, purification, and characterization

The methanol was obtained from Alphatec with 99.8% purity by mass, glycerin was obtained from Merck with 85% purity by mass, and Brazil nut oil was obtained from Amazon Oil (Belém – PA, Brazil). These chemicals were used without further purification.

The oil was converted into methyl esters by transesterification with methanol by using sodium hydroxide (NaOH) as catalyst. The amount used was 12% mole of catalyst, with a 1:6 oil:methanol molar ratio. The reaction was carried out at 338.15 K for 30 min and stirred at 600 rpm according to the methodology proposed by Barnwal and Sharma [6], Meher et al. [7], and Machado et al. [8].

The biodiesel obtained was washed four times with distilled water at 1:1 proportion at 333.15 K in order to remove the catalyst, and then dried for 24 h at 353.15 K to remove the water. Finally, the mixture was filtered with a paper filter [9].

The fatty acid content in the biodiesel was determined by High Performance Size Exclusion Chromatography (HPSEC), following the official AOCS Cd method 22:91 [10]. The fatty acids were quantified by using a Perkin Elmer Series 200 liquid chromatograph equipped with a refractive index detector (Waters 2414) using two columns: first a Jordi Gel DVB 300 × 7.8 mm, 500 A, and afterwards a JORDI DVB GEL 300 × 7.8 mm, 100 A, both using tetrahydrofuran (THF) as mobile phase (1 mL min^{-1}). The volume injected was 20 µl and the sample was diluted until 1.0% in tetrahydrofuran.

2.2. Binodal curves: Brazil nut biodiesel + methanol + glycerin

The binodal curves were determined by the cloud-point method through titration under isothermal conditions. A 15 ml jacketed equilibrium cell, designed and developed by Stragevitch [11], was used for this procedure. The temperature was maintained with the aid of a thermostatic bath with reflux (Tecnal, TE-184) and the agitation was provided by a magnetic stirrer (MS, NE-11). The temperature was measured by a glass thermometer inside the equilibrium cell.

In order to determine the cloud point, known amounts of two components, weighed on an analytical balance accurate to 0.00001 g (Shimadzu AX200), were added to the equilibrium cell and the mixture was titrated with the third component until the cloud point was obtained visually, following the procedure described by Silva et al. [12].

2.3. Tie-lines: Brazil nut biodiesel + methanol + glycerin

In order to determine the tie-lines, five different ternary mixtures were selected, with overall mass fractions defined within the immiscibility region delimited by the binodal curves. Each of the ternary mixtures was subjected to stirring for 3 h with a magnetic stir bar and was allowed to rest for at least 24 h in order to promote complete phase separation. Finally, a sample of each phase was withdrawn with the aid of a syringe and needle to measure density (digital densitometer DMA 5000, Anton Paar, accuracy 10^{-6}) and refractive index [13] (digital refractometer RE40D, Mettler Toledo, accuracy 10^{-4}).

The compositions of each component for the ternary systems were determined by using the combination of two indirect measures: density and refractive index. The compositions of all components of the system were determined by solving a system of equations formed by the empirical equations of the calibrations curves and the sum of mole fractions of all components. The first step consists in obtaining calibrations curves for each property. The calibrations curves for the densimeter and refractive index were built by cloud point procedure. Several samples of known compositions were prepared, and then density and refractive index were measured at fixed temperatures. The calibration for the densimeter was done with distilled water and dry air at $T = 298.15$ K. The digital refractometer calibration was done by measuring the refractive index of distilled water at $T = 298.15$ K and checked every week. The ternary mixtures were prepared gravimetrically in which the mass of each component of the mixture was obtained using a Shimadzu (model AX200) mass balance with an accuracy $\pm 10^{-4}$ g. These experiments were carried out according to the methodology previously presented [13].

2.4. Quality of the experimental data

As a result of Brazil nut biodiesel be a specific mixture of monoalkyl esters, the experimental methodology cannot be validated by comparing the obtained data with similar systems presented in the literature. However, there are three major components coincident in *J. curcas* biodiesel and Brazil nut biodiesel, in reasonably close proportions [14]. Therefore, comparison of data from this study to literature data of *J. curcas* biodiesel + methanol + glycerin system could be instructive and serves as an indicator of the quality of the data presented in this study.

Moreover, to ascertain the data reliability from the tie-lines, the Othmer–Tobias correlation [15] was used since no consistency test can be used in liquid–liquid equilibrium. The use of such correlation was demonstrated by Andrade et al. [16] and its linearity indicates the quality of the data with correlation given by:

$$\ln\left(\frac{1-W_{11}}{W_{11}}\right) = A + B * \ln\left(\frac{1-W_{nn}}{W_{nn}}\right) \quad (1)$$

where W_{11} is the biodiesel mass fraction (1) in the biodiesel-rich phase and W_{nn} corresponds to the glycerin mass fraction (3) in the glycerin-rich phase, A and B are the linear and angular coefficients of the straight-line expression.

2.5. Thermodynamic modeling

The experimental results of this study were used to estimate parameters for the NRTL [17] and UNIQUAC [18] activity coefficient models. Experimental tie-line compositions were inserted into the Fortran TML-LLE code [19] and the binary interaction parameters were determined by minimizing the difference between experimental concentrations and those calculated for all tie-lines of each system, according to the objective function, *S*, given by:

$$S = \sum_{k}^{D}\sum_{j}^{M}\sum_{i}^{N-1}\left\{\left(x_{ijk}^{I,exp} - x_{ijk}^{I,calc}\right)^2 + \left(x_{ijk}^{II,exp} - x_{ijk}^{II,calc}\right)^2\right\} \quad (2)$$

where *D* is the data set number, *N* and *M* are the number of components and tie-lines for each data set, respectively, superscript *I* and *II* refer to the two liquid phases in equilibrium, while superscript *'exp'* and *'calc'* refer to experimental and calculated molar fractions.

With parameters calculated by the procedure above, comparisons between experimental and calculated compositions of each component in each of the two phases were made through the mean quadratic deviation, given by:

$$\delta_x = 100\sqrt{\frac{\sum_{i}^{M}\sum_{j}^{N-1}\left(x_{ij}^{I,exp} - x_{ij}^{I,calc}\right)^2 + \left(x_{ij}^{II,exp} - x_{ij}^{II,calc}\right)^2}{2MN}} \quad (3)$$

3. Results

3.1. Experimental

The Brazil nut biodiesel obtained was characterized and compared with the Brazilian National Petroleum Agency (ANP) specifications, according to Table 1. All results are in accordance with the norm with the exception of the water content, which can be graded by improving the biodiesel's drying time.

The composition of fatty acid methyl esters (FAME) of the Brazil nut biodiesel and *J. curcas* biodiesel are presented in Table 2. As can be seen in Table 2, Brazil nut biodiesel and *J. curcas* biodiesel have the same three major components. In Fig. 1, can be observed that the systems Brazil nut biodiesel + methanol + glycerin and *J. curcas* biodiesel + methanol + glycerin exhibit partial miscibility regions very close and the slopes of the tie-lines are very similar. Minor deviations are attributed to different percentages of the three major components in different biodiesels and equilibrium data are at different temperatures, 303.15 K and 318.15 K.

Table 1
Biodiesel physicochemical characterization according to ANP.

Characteristic	Unit	Brazil nut biodiesel	ANP 07 norm
Aspect	–	Limpid	Limpid
Specific mass at 293.15 K	kg/m^3	876.96	850–900
Kinematic viscosity at 313.15 K	Mm^2/s	4.56	3.0–6.0
Water content	mg/kg	655.0	500
Flash point, min[a]	K	443.45	373.15
Ester content	mass%	97.1	96.5
Acid value.max	mg KOH/g	0.15	0.50
Diacylglycerol	mass%	1.50	Note
Triacylglycerol	mass%	1.40	Note
Methanol or ethanol.max	mass%	*	0.2
Iodine content	g/100 g	95.3	Note
Refractive index	–	1.4512	–
Saponification number	mg KOH/g	192.88	–

[a] When the analysis result in flashpoint above 373.15 K, is released analyzing content of methanol or ethanol.

Table 2
Fatty acids methyl esters (FAME) profile of biodiesel.

Number of carbons	Fatty acids	Concentration (%m/m)	
		Brazil nut	Jatrop a[a]
C12:0	Lauric	0.04	–
C14:0	Myristic	0.1	0.37
C15:0	Pentadecanoic	0.04	
C16:0	Palmitic	15.03	13.34
C16:1	Palmitoleic	0.35	0.99
C17:0	Margaric	0.07	
C17:1	cis-10 Heptadecenoic	0.04	
C18:0	Stearic	10.14	4.91
C18:1	Oleic	42.53	32.03
C18:2	Linoleic	31.04	45.05
C18:3	Linolenic	0.09	0.23
C20:0	Arachidic	0.29	0.16
C20:1	Eicosenoic	0.09	
C22:0	Behenic	0.08	
C24:0	Lignoceric	0.08	

[a] Zhou et al. [14].

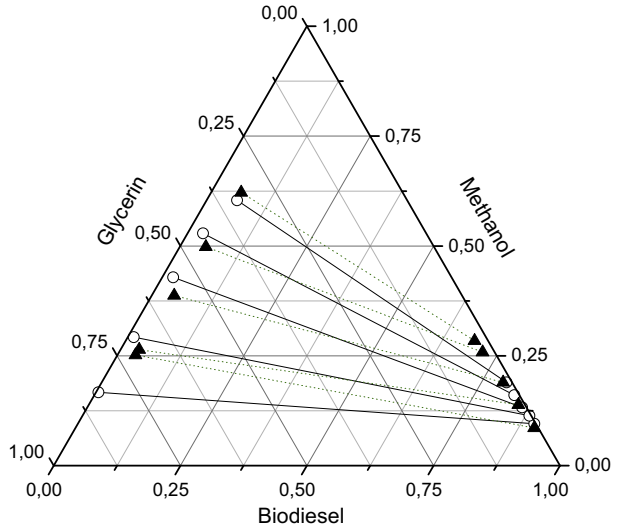

Fig. 1. Liquid–liquid equilibria of Brazil nut biodiesel at 303.15 K (○) and *Jatropha curcas* biodiesel + methanol + glycerin at 318.15 K (▲) (Zhou et al., 2006).

Fig. 2 shows that the binodal curves of Brazil nut biodiesel + methanol + glycerin system plotted through the cloud-point method at 303.15 K and 323.15 K did not significantly vary regarding the solubility of the components studied. It also shows that the immiscibility regions comprise virtually all concentration ranges of the systems studied; hence the components can be easily separated. This partial miscibility data are presented in Table 3.

Figs. 3 and 4 show that the tie lines obtained had a good agreement with the binodal curve since their end points follow the curve's trend and also cross the mixture point (overall composition). This equilibrium data are presented in Table 4.

The Othmer–Tobias correlation results showed that the experimental data were consistent, with good correlation coefficients as shown in Fig. 5 and Table 5.

3.2. Thermodynamic modeling

In the estimation procedure, biodiesel was considered a single component, whose mean molecular weight was calculated taking

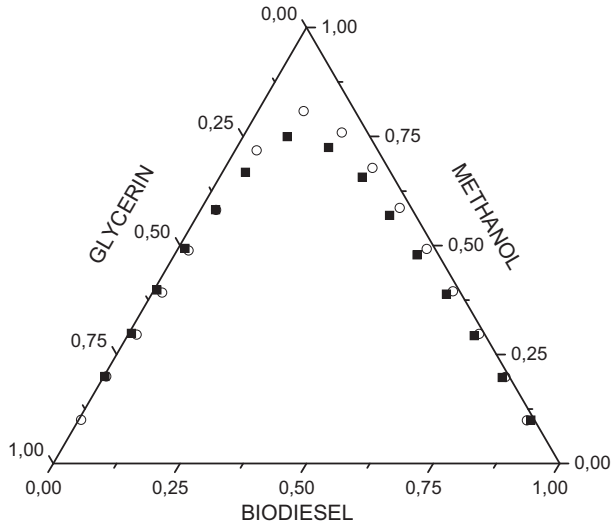

Fig. 2. Temperature effect on solubility curve of biodiesel (1) + methanol (2) + glycerin (3) system at 303.15 K (○) and 323.15 K (■).

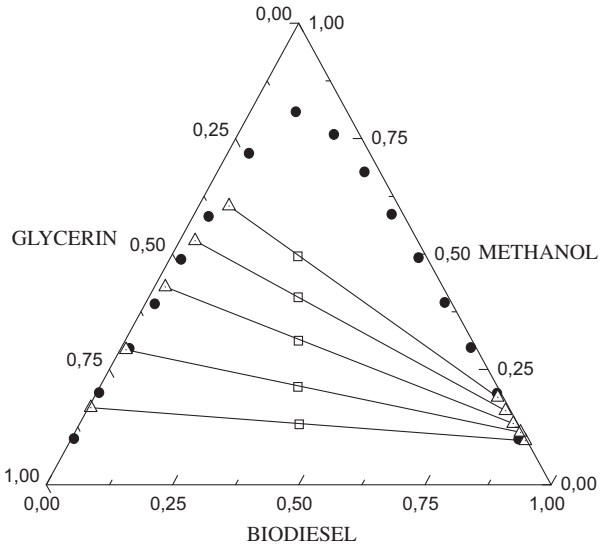

Fig. 3. Phase diagram with cloud point (●), feed (□) and tie lines (△) at 303.15 K.

Table 3
Binodal curves from biodiesel (1) methanol (2) glycerin (3) at 303.15 and 323.15 K.

w_1	w_2	w_3	Density (g/cm^3)	Refractive index
T = 303.15 K				
0.8859	0.0989	0.0152	0.867465	1.4424
0.7933	0.1987	0.0080	0.856518	1.4417
0.6947	0.2980	0.0073	0.847895	1.4395
0.5920	0.3948	0.0132	0.843626	1.4338
0.4882	0.4879	0.0239	0.835591	1.4174
0.3908	0.5864	0.0228	0.835468	1.4101
0.2911	0.6780	0.0309	0.822086	1.3803
0.1901	0.7592	0.0507	0.837478	1.3541
0.0902	0.8062	0.1036	0.835591	1.3528
0.0422	0.7183	0.2395	0.877067	1.3623
0.0307	0.5813	0.3880	0.941433	1.3790
0.0228	0.4884	0.4888	0.981678	1.3860
0.0189	0.3922	0.5889	1.021669	1.3966
0.0171	0.2952	0.6877	1.065524	1.4095
0.0052	0.0999	0.8950	1.162039	1.4373
0.0048	0.1995	0.7957	1.112297	1.4228
T = 323.15 K				
0.8935	0.0995	0.0070	0.849274	1.4347
0.7881	0.1971	0.0148	0.839162	1.4344
0.6849	0.2932	0.0219	0.837753	1.4348
0.5820	0.3886	0.0294	0.837424	1.4336
0.4791	0.4785	0.0424	0.823152	1.4325
0.3793	0.5691	0.0516	0.809476	1.4246
0.2817	0.6567	0.0616	0.81092	1.4211
0.1811	0.7247	0.0942	0.815367	1.4111
0.0871	0.7499	0.1630	0.832885	1.3487
0.0454	0.6680	0.2866	0.879433	1.3605
0.0295	0.5822	0.3883	0.91834	1.3765
0.0132	0.4933	0.4935	0.960953	1.3865
0.0055	0.3979	0.5966	1.004969	1.4257
0.0048	0.2987	0.6965	1.050157	1.4022
0.0022	0.1996	0.7982	1.098557	1.4180

into account only fatty acids at a proportion greater than 0.5%. The biodiesel's mean molecular weight was 291.62 g mol^{-1}.

3.2.1. NRTL model

Table 6 shows NRTL interaction parameters, while Table 7 shows the mean deviations obtained for the modeling at the two temperatures.

Figs. 6 and 7 show that the correlated tie-lines pass through the feed point and represent the extremes well. The model had good

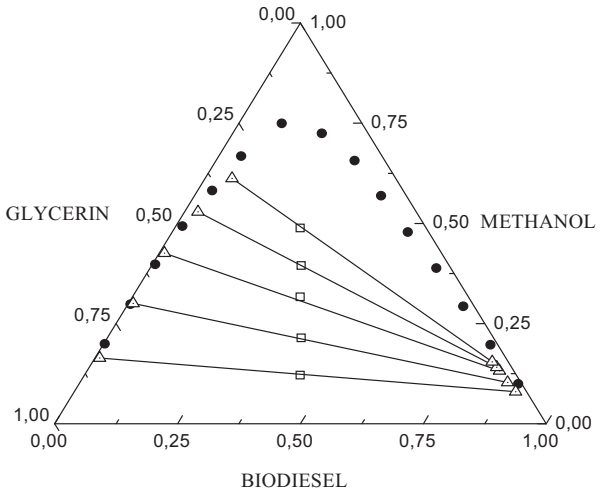

Fig. 4. Phase diagram with cloud point (●), feed (□) and tie lines (△) at 323.15 K.

agreement with the experiments, with a mean quadratic deviation of 1.49% for the system at 303.15 K and 1.18% for the system at 323.15 K.

3.2.2. UNIQUAC model

The van der Waals volume (r_i) and surface area (q_i) UNIQUAC parameters for biodiesel were calculated by Eqs. (4) and (5), which consider biodiesel composition, based on what was proposed by Batista et al. [20]. Such parameters were calculated taking into account the most significant methyl esters in Brazil nut biodiesel (palmitic, stearic, oleic, and linoleic); their values are provided in Table 8. The group volume (R_k) and area (Q_k) were taken from Magnussen et al. [21].

$$r_i = \sum_j^C w_j \sum_k^G \nu_k^{(i)} R_k \tag{4}$$

$$q_i = \sum_j^C w_j \sum_k^G \nu_k^{(i)} Q_k \tag{5}$$

Table 4
Experimental tie-lines (mass fraction) for biodiesel (1) + methanol (2) + glycerin (3) system at 303.15 and 323.15 K.

Feed			Biodiesel phase			Glycerin phase		
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
T = 303.15 K								
0.4358	0.1307	0.4335	0.9015	0.0956	0.0029	0.0048	0.1669	0.8284
0.3923	0.2120	0.3957	0.8827	0.1135	0.0038	0.0120	0.2924	0.6956
0.3433	0.3120	0.3447	0.8587	0.1324	0.0089	0.0212	0.4289	0.5499
0.2959	0.4061	0.2980	0.8294	0.1604	0.0102	0.0305	0.5287	0.4408
0.2510	0.4952	0.2537	0.8000	0.1892	0.0108	0.0600	0.6042	0.3358
T = 323.15 K								
0.4389	0.1211	0.4400	0.8980	0.0800	0.0220	0.0098	0.1639	0.8263
0.3957	0.2111	0.3932	0.8700	0.1030	0.0270	0.0099	0.3000	0.6901
0.3411	0.3168	0.3421	0.8389	0.1320	0.0291	0.0105	0.4259	0.5636
0.3041	0.3944	0.3015	0.8288	0.1411	0.0301	0.0275	0.5289	0.4436
0.2554	0.4882	0.2564	0.8127	0.1548	0.0325	0.0550	0.6123	0.3327

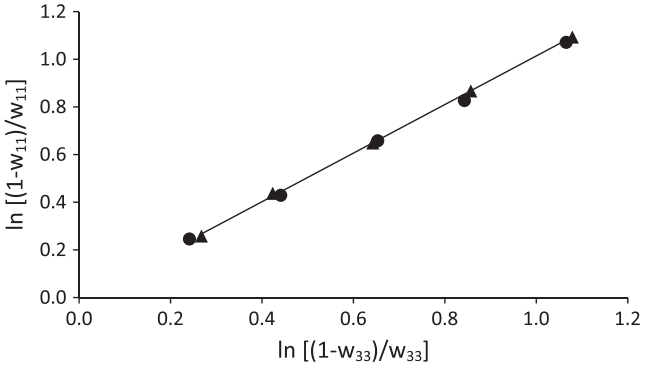

Fig. 5. Othmer–Tobias plot for biodiesel (1) + methanol (2) + glycerin (3) system at 303.15 K [▲] and 323.15 K [●].

Table 5
Results obtained for A, B and R^2 for the Othmer–Tobias correlation.

Systems	A	B	R^2
Biodiesel + methanol + glycerin at 303.15 K	−0.0059	1.02	0.9995
Biodiesel + methanol + glycerin at 323.25 K	−0.0024	0.9998	0.9989

Table 6
NRTL parameters.

Pair i–j	A_{ij}	A_{ji}	α_{ij}
Biodiesel–methanol	−1.4456	3665.1	0.28800
Biodiesel–glycerin	757.33	1852.7	0.20001
Methanol–glycerin	392.68	0.7703	0.20000

Table 7
NRTL mean deviations of each tie line.

Tie lines	Mean deviation (%)
T = 303.15 K	
1	1.58
2	1.69
3	1.82
4	0.88
5	1.27
Mean quadratic deviation	1.49
T = 323.15 K	
1	1.28
2	1.19
3	0.97
4	1.07
5	1.37
Mean quadratic deviation	1.18

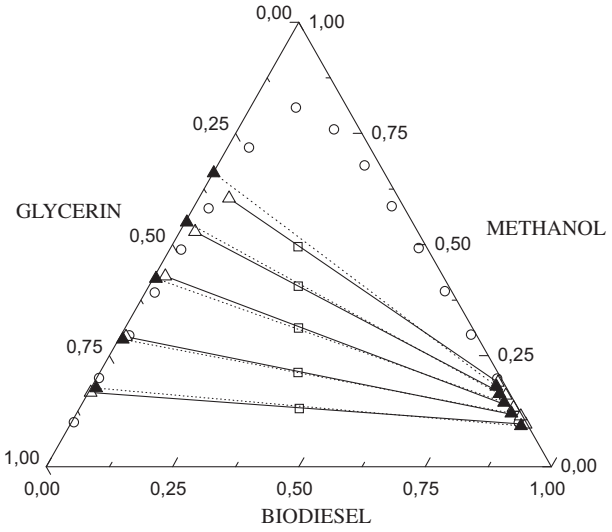

Fig. 6. LLE (mass fraction) for biodiesel (1) + methanol (2) + glycerin (3) system at 303.15 K. Experimental (Δ), feed (□), cloud-point (○) and NRTL (▲).

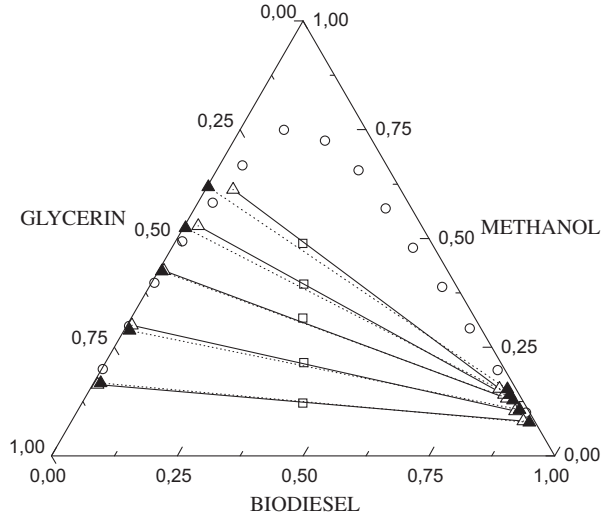

Fig. 7. LLE (mass fraction) for biodiesel (1) + methanol (2) + glycerin (3) system at 323.15 K. Experimental (△), feed (□), cloud-point (○) and NRTL (▲).

where w_i is the fatty acid's methyl percentage and v_k is the number of groups of type k in molecule i.

Table 8
UNIQUAC parameters r_i and q_i.

Component	r_i	q_i
Biodiesel	13.2519	10.6895
Methanol	1.4311	1.432
Glycerin	4.7957	4.908

Table 9
UNIQUAC binary interaction parameters for biodiesel + methanol + glycerin.

Pair *i–j*	A_{ij}	A_{ji}
Biodiesel–methanol	−210.45	2996.4
Biodiesel–glycerin	200.44	200.21
Methanol–glycerin	−254.15	103.82

Table 10
UNIQUAC mean deviations of each tie line.

Tie lines	Mean deviation (%)
T = 303.15 K	
1	3.22
2	1.06
3	2.02
4	0.97
5	0.75
Mean quadratic deviation	1.85
T = 323.15 K	
1	2.01
2	1.46
3	1.46
4	2.35
5	2.36
Mean quadratic deviation	1.97

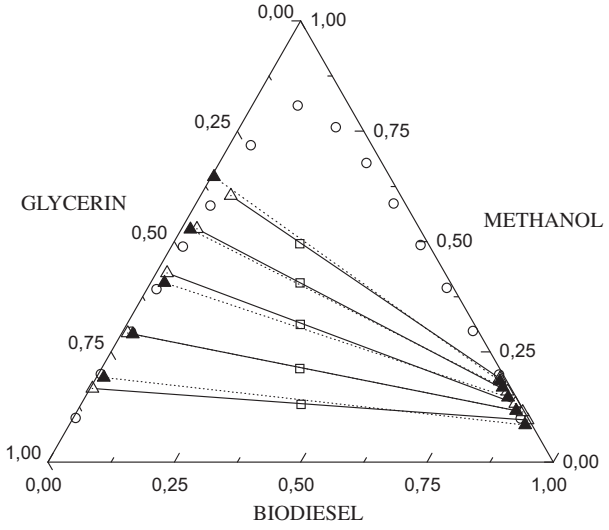

Fig. 8. LLE (mass fraction) for biodiesel (1) + methanol (2) + glycerin (3) system at 303.15 K. Experimental (△), feed (□), cloud-point (○) and UNIQUAC (▲).

Table 9 shows the molecular interaction parameters set for the UNIQUAC model.

The UNIQUAC model also had a good agreement with the experimental data, with a mean quadratic deviation of 1.85% for the system at 303.15 K and 1.97% for the system at 323.15 K. Deviations can be seen in Table 10, and the results in Figs. 8 and 9.

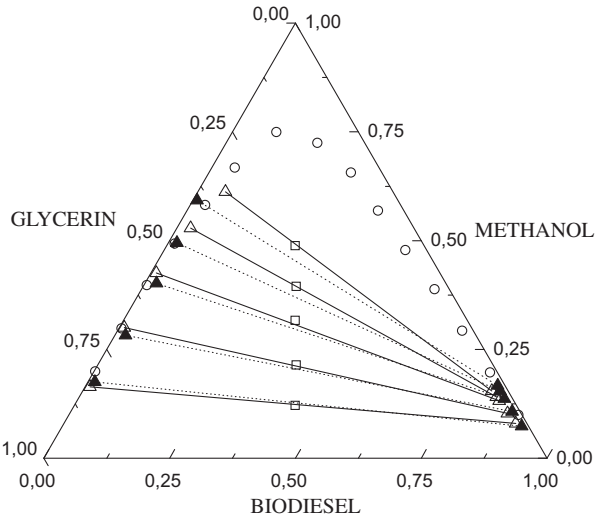

Fig. 9. LLE (mass fraction) for biodiesel (1) + methanol (2) + glycerin (3) system at 323.15 K. Experimental (△), feed (□), cloud-point (○) and UNIQUAC (▲).

4. Conclusions

The transesterification reaction of Brazil nut oil with methanol was easily carried out, reaching a methyl ester conversion of 97%, without the need for a second reaction. Physicochemical tests showed that the biodiesel obtained was within the standards established by the ANP.

The binodal curves showed that, at 303.15 and 323.15 K, there is no significant variation in the solubility of the components studied and that the immiscibility region covers most of the diagram. Thus, the separation of these components is feasible.

The tie-lines indicated a good agreement with the binodal curve, demonstrating the quality of the data. As a further ascertaining of this quality, the well-known Othmer–Tobias correlation was applied showed high linearity, which again indicates the good quality of the data.

The experimental data were correlated with the NRTL and UNIQUAC activity coefficient models, the results were in good agreement with the experimental data, with a mean quadratic deviation in the composition of 1.49% at 303.15 K and 1.18% at 323.15 K for NRTL, and 1.85% and 1.97% for UNIQUAC at the same temperatures, respectively.

Acknowledgements

The authors are grateful to CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil) and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil) for the financial support.

References

[1] Rostami M, Sona R, Maziyar M, Masoud N. Liquid–liquid equilibria in biodiesel production. J Am Oil Chem Soc 2012;90:147–54.
[2] Bell JC, Messerly RA, Gee R, Harrison A, Rowley RL, Wilding WV. Ternary liquid–liquid equilibrium of biodiesel compounds for systems consisting of a methyl ester + glycerin + water. J Chem Eng Data 2013;58:1001–4.
[3] Basso RC, Silva CAS, Sousa CO, Meirelles AJA, Batista EAC. LLE experimental data, thermodynamic modeling and sensitivity analysis in the ethyl biodiesel from macauba Pulp oil settling step. Bioresour Technol 2013;131:468–75.
[4] Mazutti MA, Voll FAP, Cardozo-Filho L, Corazza ML, Lanza M, Priamo WL, et al. Thermophysical properties of biodiesel and related systems: (liquid+liquid) equilibrium data for soybean biodiesel. J Chem Thermodyn 2013;58:83–94.
[5] Silva JRF, Mazutti MA, Voll FAP, Cardozo-Filho L, Corazza ML, Lanza M, et al. Thermophysical properties of biodiesel and related systems: (liquid+liquid) equilibrium data for *Jatropha Curcas* biodiesel. J Chem Thermodyn 2013;58:467–75.

[6] Barnwal BK, Sharma MP. Prospects of biodiesel production from vegetable oils in India. Renew Sustain Energy Rev 2005;9:363–78.
[7] Meher LC, Vidya Sagar D, Naik SN. Technical aspects of biodiesel production by transesterification—a review. Renew Sustain Energy Rev 2006;10:248–68.
[8] Machado AB, Ardila YC, Oliveira LH, Aznar M, Maciel MRW. Liquid−liquid equilibria in ternary and quaternary systems present in biodiesel production from soybean oil at (298.2 and 333.2) K. J Chem Eng Data 2012;57:1417–22.
[9] Franca BB, Pinto FM, Pessoa FLP, Uller AMC. Liquid–liquid equilibria for castor oil biodiesel + glycerol + alcohol. J Chem Eng Data 2009;54:2359–64.
[10] American Oil Chemist's Society. Official methods recommended practices of the AOCS. Champaign: AOCS; 2009.
[11] Stragevitch L. Equilíbrio líquido–líquido de misturas de não eletrólitos. 398f. Tese (Doutorado) – Universidade Estadual de Campinas, Faculdade de Engenharia Química, Campinas, 1997.
[12] Silva S, Mafra MR, Silva MR, Ndiaye PM, Ramos LP, Cardozo Filho L, et al. Liquid–liquid and vapor–liquid equilibrium data for biodiesel reaction-separation systems. Fuel 2013;108:269–76.
[13] Rocha EGA, Romero LAF, Duvoisin JS, Aznar M. Liquid–liquid equilibria for ternary systems containing ethylic palm oil biodiesel + ethanol + glycerol/water: experimental data at 298.15 and 323.15 K and thermodynamic modeling. Fuel 2014;128:356–65.
[14] Zhou H, Lu H, Liang B. Solubility of multicomponent systems in the biodiesel production by transesterification of *Jatropha curcas* L. oil with methanol. J Chem Eng Data 2006;51:1130–5.
[15] Othmer TF, Tobias PE. Tie line correlation. Ind Eng Chem 1942;34:693–6.
[16] De Andrade VM, Rodrigues GD, Carvalho RMM, Silva LHM, Silva MCH. Aqueous two-phase systems of copolymer L64 + organic salt + water: enthalpic L64–salt interaction and Othmer–Tobias, NRTL and UNIFAC thermodynamic modeling. Chem Eng J 2011;171:9–15.
[17] Renon H, Prausnitz JM. Local compositions in thermodynamic excess functions for liquid mixtures. AIChE J 1968;14:135–44.
[18] Abrams DS, Prausnitz JM. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. AIChE J 1975;21:116–28.
[19] Stragevitch L, d'Avila SG. Application of a generalized maximum likelihood method in the reduction of multicomponent liquid–liquid equilibrium data. Brazilian J Chem Eng 1997;14:41–52.
[20] Batista E, Monnerat S, Kato K, Stragevitch L, Meirelles AJA. Liquid–liquid equilibrium for systems of canola oil, oleic acid and short-chain alcohols. J Chem Eng Data 1999;44:1360–4.
[21] Magnussen T, Rasmussen P, Fredenslund Aa. UNIFAC parameter table for prediction of liquid–liquid equilibria. Ind Eng Chem Process Des Dev 1981;20:331–9.